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Investigation of low frequency dynamic viscoelastic properties of aqueous polyethylene oxide solutions

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INVESTIGATION OF LOW FREQUENCY DYNAMIC
VISCOELASTIC PROPERTIES OF AQUEOUS
POLYETHYLENE OXIDE SOLUTIONS

JOHN W. KINNIER
and
WALTER A. REISTER

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by

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Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

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ABSTRACT

Some of the viscoelastic properties of aqueous solutions of polyethylene oxide were studied using a torsional pendulum method in the low audio frequency range. Measurement of the decay constant and the changes in resonant frequency of the mechanical oscillator pendulum due to mechanical loading caused by contact with the solutions permitted calculation of the components of the complex viscosity (or complex shear modulus). Comparison is made with viscosity determinations from rotating spindle and capillary tube viscometers. A relaxation in the viscoelastic properties is observed in this frequency range which cannot be described by a simple Maxwell model. This behavior suggests that a distribution of relaxation frequencies will be required to give an adequate description of the viscoelastic properties in these solutions.

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a = radius of inertial weight

A = area of fluid contact with oscillator

b = radius of torsional rod

C = constant for converting between Z and Z_f for given oscillator

f = frequency in cycles per second

G = modulus of elasticity

$G*$ = complex modulus of elasticity

G_1 = real part of $G*$

G_2 = imaginary part of $G*$

h = height of inertial weight

I = moment of inertia

K_α = decay rate constant

K_ω = frequency constant

l = length of torsional rod

r = radial distance from axis of rotation of oscillator

R = specific mechanical resistance due to fluid

R_f = total mechanical resistance due to fluid

R_i = internal motional resistance of unloaded oscillator

S = torsional spring constant

x, y, z = mutually perpendicular coordinate system

X = specific mechanical reactance due to fluid

X_f = total mechanical reactance due to fluid

Z = specific mechanical impedance due to fluid

Z_f = total mechanical impedance due to fluid

α = temporal decay constant

α_o = temporal decay constant for unloaded oscillator

δ = spacial decay constant

η = coefficient of viscosity

η^* = complex coefficient of viscosity

η_1 = real part of η^*

η_2 = imaginary part of η^*

η_a = apparent viscosity

ρ = density

μ = torsional shear modulus

ω = angular frequency

ω_0 = mechanical resonant angular frequency of oscillator

1. Introduction

Polyethylene oxide dissolved in water is known to form polymer
solutions which possess certain anomalous physical properties (2,7).
These solutions are classed as being "viscoelastic," i.e. the result-
ing liquids display both viscous and elastic properties. These solu-
tions also show a "non-Newtonian" viscous property called "pseudo-
plasticity," which is a rheological designation applied to fluids
which demonstrate an apparent decrease in viscosity with increasing
rates of shear. Figure 6 indicates this property.

The chemical formula for polyethylene oxide is $(-CH_2-CH_2-O-)_n$.
This linear molecule is known to form very long chains in solution.
The resin used to make the solutions investigated was produced by the
Union Carbide Company, and has the trade name POLYOX WSR-301. The
approximate weight-average molecular weight is 4,000,000 (20).
Henceforth in this paper the term "polyox" will be used vice "poly-
ethylene oxide."

Philipoff first found the phenomonon of apparent viscosity de-
crease with increasing frequency of motion for certain fluids (15).
He also found that the viscosity of polymers under oscillating defor-
mations depends only on the frequency, and not on the amplitude of
the deformation (5). An equivalence between the angular frequency
in the measurement of dynamic viscosity and the shear rate in the
measurement of non-Newtonian viscosities using flow techniques for
certain polymer solutions has been demonstrated (14). This equivalence
has also been predicted theoretically for linear polymer solutions (5).

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Research conducted by LT Chester at this institutuion showed that in the frequency range of 10-26 megacycles per second the coefficient of absorption for plane compressional waves propagated in low concentration polyox solutions was essentially the same as that for water (7). This indicates that the viscous effects of the polymer chains are completely relaxed for these frequencies. The investigations here reported were conducted at frequencies in the range of hundreds of cycles per second in order to get some measure of this viscous relaxation and elastic properties of these solutions as a function of frequency.

The concept of a complex viscosity was proposed by Gemant (11). This representation, where $\eta^* = \eta_1 - i\eta_2$, lends itself well to the characterization of viscoelastic fluids. For a perfectly viscous fluid η_2 would be zero, whereas for a perfectly elastic fluid η_1 would be zero. Thus the relative size of η_1 and η_2 can provide a measure of the degree of viscoelasticity. However, it should be noted that while the use of a complex viscosity is valid for oscillatory flow, it is not valid for steady flow.

2. Theory of Measurement

In order to investigate the shear viscosity and shear modulus of polyox solutions in the low frqquency range of hundreds of cycles per second, it was desirable to generate a pure shear wave in the test fluid. Torsional pendulums of the type shown in Figure 2 were used for this purpose, since they provide a simple method of generating such waves in this frequency range (19). However, a separate pendulum is required for each frequency investigated. As can be seen in Figure 2, the portion of the pendulum in contact with the fluid was the sides and bottom of a circular cylinder. To simplify the derivation of the mathmatical expressions needed, it will be assumed that this cylinder can be treated as a flat plate radiating into an infinite medium. The validity of this assumption will be demonstrated once the appropriate formulas have been obtained.

Consider a flat plate in contact with a viscous fluid to be oscillating parallel to itself. Let the direction of motion be the y direction, and z be perpendicular to the plane. The Navier-Stokes equation for nonsteady parallel flow in the fluid reduces to (11):

$$\rho \frac{\partial v_y}{\partial t} = -\eta \frac{\partial^2 v_y}{\partial z^2} \ .$$

A general solution to this is

$$v_y = v_0 \, e^{-\gamma z} ,$$

where

$$\gamma = \left(i \omega \rho / \eta \right)^{\frac{1}{2}} = \left(\pi f \rho / \eta \right)^{\frac{1}{2}} \left(1 + i \right) .$$

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As an example, for a frequency of 100cps, a liquid having a density of one gram per cubic centimeter and a viscosity of ten poise, the shear wave velocity amplitude would be attenuated to 1/e of its value at the boundry at a distance of only about 1/8 centimeter from the oscillating surface. (For these investigations, the frequency used was always greater than 100cps and the viscosity of the liquids was always less than ten poise. Thus the attenuation was even greater for our experiments.) It is this very rapid spatial attenuation that justifies our initial assumption, and shows that side wall and end effects may be ignored. It also makes it necessary to measure the acoustic properties of the shear wave by its loading effect on the oscillator.

From the basic definition of viscosity, we can now write

$$F_y = - A \eta \left(\frac{\partial v_y}{\partial z} \right)_{z=0}$$

for the viscous force the fluid exerts on the cylinder. The specific acoustic load impedance (Z) is defined as the ratio of the shearing stress to the particle velocity,

$$Z = \frac{F_y / A}{v_y} \Big)_{z=0} .$$

Using the foregoing,

$$Z = \frac{- A \eta \frac{d}{dz} \left(v_0 e^{-\gamma z} \right) / A}{v_0 e^{-\gamma z}} .$$

For simple harmonic motion at an angular frequency, ω,

$$Z = \left(i \omega \rho \eta \right)^{1/2},$$

or

$$Z = \left(\pi f \rho \eta \right)^{1/2} \left(1 + i \right),$$

since

$$\sqrt{i} = \sqrt{1/2} \left(1 + i \right).$$

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We can also write

$$Z = R + iX,$$

Where R and X are the specific load resistance and reactance the fluid presents to the oscillator.

If η is now considered to be complex (η^*), as proposed by Gemant (11), we can proceed as follows:

$$\eta^* = \eta_1 - i\eta_2.$$

Then

$$Z = R + iX = (\pi f \rho \eta^*)^{1/2}(1 + i).$$

Squaring both sides,

$$(R + iX)^2 = \pi f \rho (\eta_1 - i\eta_2)(1 + 2i - 1),$$

$$R^2 - X^2 + i2RX = \omega \rho \eta_2 + i\omega \rho \eta_1.$$

Equating reals and imaginaries gives

$$R^2 - X^2 = \omega \rho \eta_2,$$
$$2RX = \omega \rho \eta_1.$$

From which

$$\eta_2 = (R^2 - X^2)/\omega \rho$$

and

$$\eta_1 = 2RX/\omega \rho.$$

Now, if R and X can be measured, η_1 and η_2 may be calculated. Note that for a Newtonian Fluid, $R = X = (\pi f \rho \eta)^{1/2}$, and $\eta_2 = 0$.

By considering only the real part (R) of the complex impedance (Z), an "apparent viscosity" η_a can be determined. As will be shown later, R is determined by decay rate measurements, and apparent viscosity is then the viscosity of a Newtonian Fluid that would cause the same decay rate as the fluid being measured.

An alternate representation would have been to use a complex

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shear modulus G*.

Where $\qquad G^* = G_1 + i\,G_2$.

η^* and G^* are interrelated by the identity $\eta^* \equiv G^*/i\omega$.
From this it can be seen that

$$\eta_1 = G_2 / \omega \qquad\qquad \omega\,\eta_1 = G_2$$

$$or$$

$$\eta_2 = G_1 / \omega \qquad\qquad \omega\,\eta_2 = G_1 \; .$$

In order to determine Z and thence η^*, the effect of a fluid
load impedance on the oscillating cylinder must be determined.
If Θ = angular displacement of the torsional oscillator, then the
differential equation for the oscillator for damped simple harmonic
motion with no driving torque is:

$$(1) \qquad I\,\ddot{\Theta} + R_i\,\dot{\Theta} + S\,\Theta = 0$$

Where I = moment of inertia of system

$\qquad R_i$ = motional resistance (friction) of system

$\qquad$ S = torsional "spring constant" of torsional rod.

The solution is (except for a phase factor):

$$\Theta = \Theta_o\, e^{-\alpha_o t}\, e^{i\omega_o t},$$

where $\quad \Theta_o$ = initial amplitude

$$\alpha_o = R_i / 2I$$

$$\omega_o = \left[S/I - (R_i/2I)^2 \right]^{1/2}.$$

From the above, the specific mechanical impedance which the fluid
adds to the system is Z = R + iX. However, the total moment of
impedance (Z_f) must be used. By definition, Z_f is the ratio of the

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torque to the angular velocity of the fluid, evaluated at the surfaces of the cylinder. Alternatively, since Z acts on the cylinder at some distance r from the axis of rotation, Z_f, the total moment of impedance presented by the fluid can also be determined by the relation (16):

$$Z_f = Z \cdot C,$$

where C is constant for a given cylinder. The evaluation of C must take into account the areas of the cylinder in contact with the fluid as a function of the distance (r) from the axis of torsional oscillations. Now the equation of motion for the cylinder in contact with a fluid becomes:

$$I \ddot{\theta} + (R_i + Z_f) \dot{\theta} + S\theta = 0$$

or

$$\ddot{\theta} + \left(\frac{R_i + Z_f}{I}\right) \dot{\theta} + \frac{S}{I}\theta = 0.$$

This still has a solution of the form

$$\theta = \theta_o e^{-\alpha t} e^{i\omega t} = \theta_o e^{-(\alpha - i\omega)t}.$$

Putting this solution into the differential equation and letting $\beta = \alpha - i\omega$ gives for β:

$$\beta = \frac{R_i + Z_f}{2I} \pm i \left[\frac{S}{I} - \left(\frac{R_i + Z_f}{2I}\right)^2\right]^{1/2}.$$

Putting in $Z_f = R_f + iX_f$ gives:

$$\beta = \frac{R_i + R_f}{2I} + i\frac{X_f}{2I} \pm i\left[\frac{S}{I} - \left(\frac{R_i + R_f + iX_f}{2I}\right)^2\right]^{1/2},$$

and then on expanding and rearranging,

$$\beta = \frac{R_i + R_f}{2I} + i\frac{X_f}{2I} \pm i\left\{\left[\frac{S}{I} - \left(\frac{R}{2I}\right)^2\right] - \left[\frac{R_f(R_i + R_f) - X_f^2}{4I^2} + i\frac{2X_f(R_i + R_f)}{4I^2}\right]\right\}^{1/2}.$$

Now, to simplify writing, we eliminate negative frequencies by dropping the minus sign in front of the square root term, and letting

$$\omega_o^2 = \left[S/I - \left(\frac{R_i}{2I} \right)^2 \right],$$

$$\alpha_o = \frac{R_i}{2I},$$

and

$$\delta^2 = \left[\frac{R_f (R_i + R_c) - X_f^2}{4 I^2} + i \frac{2 X_f (R_i + R_c)}{4 I^2} \right].$$

Then,

$$\beta = \alpha_o + \frac{R_f}{2I} + i \frac{X_f}{2I} + i \left[\omega_o^2 - \delta^2 \right]^{1/2},$$

or

$$\beta = \alpha_o + \frac{R_f}{2I} + i \frac{X_f}{2I} + i \omega_o \left[1 - \delta^2/\omega_o^2 \right]^{1/2}.$$

Using a binomial expansion of the term in brackets gives:

$$i \omega_o \left[1 - \delta^2/\omega_o^2 \right]^{1/2} = i \omega_o \left[1 + \delta^2/2\omega_o^2 - \frac{1}{8} \left(\delta^2/\omega_o^2 \right)^2 + \cdots \right],$$

or

$$i \omega_o \left[1 - \delta^2/\omega_o^2 \right]^{1/2} = i \left[\omega_o + \delta^2/2\omega_o - \frac{1}{8} \delta^4/\omega_o^3 + \cdots \right].$$

Since δ^2/ω_o is at least six orders of magnitude smaller than ω_o and at least three orders of magnitude smaller than any other terms in β, only the first term of the expansion need be retained.
Then,

$$\beta = \alpha_o + \frac{R_f}{2I} + i \left[\omega_o + X_f/2I \right]$$

or

$$\alpha - i \omega = \alpha_o + R_f/2I + i \left[\omega_o + X_f/2I \right].$$

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Equating reals and imaginaries gives,

$$\alpha = \alpha_o + R_f / 2I$$

and

$$-\omega = \omega_o + X_f / 2I$$

Solving these for R_f and X_f, we have,

$$R_f = 2I(\alpha - \alpha_o) = 2I \Delta\alpha$$

and

$$X_f = 2I(\omega_o - \omega) = 2I \Delta\omega .$$

However, $R_f = R \cdot C$ and $X_f = X \cdot C$,

and then

$$R = \frac{2I}{C} \Delta\alpha \quad and \quad X = \frac{2I}{C} \Delta\omega .$$

Letting $\dfrac{C}{2I} = K_\alpha = K_\omega ,$

then

$$\boxed{R = \frac{\Delta\alpha}{K_\alpha}} \quad and \quad \boxed{X = \frac{\Delta\omega}{K_\omega}} .$$

These equations are used to calculate the loading impedance the
fluids present to the oscillator. In theory, $K_\alpha = K_\omega$, and in principle
they can be calculated. In practice, K_α and K_ω were determined exper-
imentally by loading the oscillator with Newtonian fluids of known
viscosity, and K_α and K_ω were calculated from values of $\Delta\alpha$ and $\Delta\omega$
measured. The values obtained are given in Table 3. It is to be
noted that K_α and K_ω are very nearly equal in all cases.

To complete the theoretical determination of K_α and K_ω requires
a method of calculating C for each oscillator. The moment of impedance
due to the fluid (Z_f) is related to the specific impedance (Z) by

$$Z_f = \int Z r^2 dA$$

where the integral is taken over the area of fluid contact. Here it is seen that

$$C = \int r^2 dA .$$

The fluid to be tested was in contact with the bottom and sides of the lower inertial mass. (See Figure 2.) Let

a = radius of inertial mass

and h = height of inertial mass

then

$$C = \int r^2 dA = 2\pi a^3 \int_0^h dh + 2\pi \int_0^a r^3 dr,$$

where the first term on the right is due to the side loading and the second term is due to the bottom loading of the fluid.

Integrating gives

$$C = 2\pi a^3 \left(h + a/4 \right).$$

Then

$$Z_f = 2\pi a^3 \left(h + a/4 \right) Z .$$

From this it can be seen that, theoretically,

$$K_\alpha = K_\omega = \pi a^3 \left(h + a/4 \right) / I .$$

The moment of inertia can be calculated with relative ease from the dimensions and masses of the various components of the oscillator, and C is also easily calculated. These calculations of K_α and K_ω did not agree with those measured experimentally. There are several reasons for this lack of agreement. One is the strong possibility that the clamp at the center of the torsional rod was not completely

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successful in forcing a node at that point. Another is the uncertainty in the effective position of the boundary between the torsional rod and the attached inertial weights.

Also, as can be seen in Table 3, the theoretical prediction that K_λ would equal K_ω was not exactly realized in the experiment. The most likely explanation for the small disagreement between theory and experiment lies in the difference in the method for measurement of K_λ and K_ω. K_α was determined from measurements made while the oscillations were actually decaying, but K_ω was determined while the oscillations were being maintained at a specified level. Furthermore, tests on the oscillators showed that their decay rate and resonant frequency during decay, even while not loaded by the fluid, was dependent on both initial amplitude, and amplitude during measurement. Such a system can be thought of as having an apparent inertia which is slightly amplitude dependent. This apparent inertia combined with the difference in technique for measurements could account for the fact that the K's were not exactly equal.

3. Measurements

The pendulums were calibrated by measuring $\Delta\alpha$ and $\Delta\omega$ in standard Newtonian liquids of known viscosity and density. Thus it is possible to plot $\Delta\alpha$ versus R and $\Delta\omega$ versus X for these standards, and the slope of the resulting straight line is then K_α and K_ω, respectively, for that pendulum. (Note, X = R for Newtonian Fluids.) Typical calibration plots may be seen in Figure 5. (In practice, the equation of the best fitting straight line was determined using a least-square-error technique (3). A digital computer was utilized for this purpose, as well as an aid in reducing other data.)

It was not possible to measure with sufficient accuracy the frequency of an oscillator under the conditions of equation (1), i.e. a freely decaying system. The frequency of free oscillations should be the frequency of mechanical resonance, or the frequency at which a driving force will supply maximum power to the oscillator (13). To determine this frequency each oscillator was driven at a fixed reference level, using electro-mechanical feedback. The phase of the driving system was then adjusted so that minimum power was delivered to the driving coils to maintain this level. The frequency was then measured.

It was found that the decay characteristics of the oscillators were not precisely as predicted by equation (1). The oscillations did not decay exactly exponentially over the entire range of decay, and the rate of decay was affected by the initial amplitude. In order to standardize the procedure so that the effect of the liquid

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loading could be accurately determined, the initial amplitude of oscillations was held constant and the decay rate was always measured over the same range.

Relative to the accuracy required for the measurement of the frequencies involved in this work, the oscillators were very sensitive to small changes in temperature. In view of this, the entire assembly was enclosed in an insulated box where the temperature was thermostatically controlled. All measurements were taken at 25.2 ±0.1 °C.

The method developed during these investigations is in principle identical to that reported by Sittel, Rouse, and Bailey (19), and the analysis is almost identical.

A more detailed description of the procedures and instrumentation used may be found in Part 4.

The apparent viscosities of the polyox solutions were also measured with a Brookfield Model LVT viscometer and with various capillary tube viscometers of the Oswald and Fenske-Cannon types (12). The Brookfield viscometer is a rotational type with which the resisting torque due to the liquid is measured as a spindle is rotated in the liquid at a constant speed. The shear rate is directly proportional to the rotational speed. The instrument is calibrated such that the viscosity can be obtained from the measured torque and the motor speed.

4. Equipment and Procedures

A. Details of Equipment and Procedure for Measurement

The response of the mechanical torsional oscillators was measured using two barium titanate transducers. These were arranged on the rim of the top of the upper oscillator, 180° apart. (See Figures 3 and 4.) One end of each was constrained to move with the oscillator, the other end was free. Their inertia during movement of the oscillator caused them to expand or contract, producing an electrical signal proportional to their acceleration. The outputs of the two transducers were put in parallel.

For decay rate and frequency measurements, the signal from the transducers was fed through a General Radio Wave Analyzer, which acted both as a filter and as an amplifier. The Wave Analyzer was also the monitoring point for transducer output. A 10cps pass band was usually employed, and the AFC mode of operation was utilized. For measuring decay rates, the "recorder" output of the Wave Analyzer was sent to a Bruel and Kjaer high speed level recorder, operated as a logarithmic recorder, which plots a record of the decay as a function of time. A 25db range was found most suitable, with the time scale varied to give a slope of about 20-50 degrees for the decay rate being measured. The oscillator was stabilized at a transducer output of 1.5mv, the drive circuit turned off, and the decay rate recorded. Usually, six decays were measured for each fluid and the results were averaged.

To measure frequency, the Wave Analyzer was set as for decay rate measurements, but the filtered output was employed. This was fed to a period counter. With transducer output stabilized at 1.5mv,

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(steady-state vibration of the pendulum), several counts of 10^3 or 10^4 periods duration were taken, and then averaged for the measurement used.

The drive system was basically a feedback system which used the oscillator as the frequency standard. (See Figure 1.) The feedback drive was adjusted in phase and amplitude, with the oscillator unloaded, to give a steady transducer output of 1.5mv, using minimum drive power.

To accomplish this, the transducer output was amplified by a high input impedance amplifier, the phase was adjusted in an RC filter network having variable R. The filter output was amplified and sent to a power amplifier with adjustable output level. This signal was then used for the driving coils of the electro-mechanical drive. The output voltage and current of the power amplifier were measured to determine the power supplied to the oscillator.

The drive unit consisted of two permanent magnets of "square"-horseshoe shape mounted on top of the oscillator 180 degrees apart, on a line about 90 degrees from the 180 degree line of the transducer mounts. The two driving coils were series connected and wound on soft iron cores. They were also "square"-horseshoe shaped to match the permanent magnets. The coils and iron cores were mounted on a fixed base above the oscillator, in such a position that the two open faces of a coil were aligned to the two open faces of a permanent magnet. (See Figure 3.) This arrangement provides an essentially sinusoidal push-pull driving force to each magnet. Tests showed that the electro-mechanical coupling was small. Provision was made to break the feedback drive system in front of the phase shifter for decay measurements.

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B. Solution Mixing Procedures

It is known that the properties of polyox solutions in water can be influenced by the mixing technique (2, 20). In general, mixers employing high shear rates decrease the apparent viscosity of the resulting solutions when compared to otherwise similar solutions mixed using lower shearing rates. This effect is attributed to a physical breaking of the longer chains at the higher shear rates. For this reason, all mixing of test solutions was done with low speed rotary mixers. In addition, a few test fluids were mixed using a boiling water method (20) for comparison with the main test solutions. No pronounced differences in the apparent viscosity was found between the normal test solutions and those mixed using the more gentle boiling method. Mixing time for the test solutions varied from one to several days, depending on concentration.

It is also known that polyox solutions may decrease in apparent viscosity with time. This so called time degradation is most probably the result of some chemical reaction which tends to break the long chains into smaller chains, thus causing a decrease in the mean molecular weight. For this reason, precautions were taken to insure that solutions tested were "fresh". This was accomplished by testing them with the Brookfield viscometer as soon as mixed and then again immediately before testing with the oscillator. If the apparent viscosity had not changed, it was assumed that no degradation had occurred. Although additives can be used to retard the oxidation of the polyox solutions, they were not used during these studies. During the experiments, the phenomenon of time degradation was observed

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in several samples. While no quantitative results were obtained, one qualitative observation was made. The time degradation effect would not be observed in a given solution for a period varing from a few days to several weeks. However, once the degradation started, it was observed to proceed rapidly.

5. Results

The primary results of the measurements obtained using the torsional oscillator are presented in terms of the components of a complex viscosity and shear modulus, and the absolute values of these quantities. These results are tabulated in Table 1. The apparent viscosities measured by these oscillators are presented in Table 2(a) and the apparent viscosities as measured by the capillary tube viscometers may be seen in Table 2(b). Figure 6 shows the apparent viscosities of the polyox solutions measured with the Brookfield viscometer.

It is felt that the quantities which best characterize the viscoelastic nature of the solutions are the real parts of the complex viscosity and shear modulus, i.e. η_1 and G_1. These two quantities give a simultaneous measure of the viscous and the elastic properties of the solutions directly. The values obtained for η_1 and G_1 are tabulated in Table 1. The results agree with relaxation theory. That is to say, the viscosity η_1 decreased with increase in frequency, and the shear modulus G_1 increased with increase in frequency. This was true for all polyox concentrations tested. These results are also plotted in Figure 9.

Figure 8 shows the change in the real and imaginary parts of complex viscosity, i.e. η_1 and η_2, as the concentration of polyox increased. This plot also shows how η_2 approaches zero, and η_1 approaches the viscosity of distilled water, as the polyox concentration approaches zero.

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The apparent viscosities of the polyox, i.e. the viscosities of
Newtonian fluids which would have caused the oscillators to decay at
the same rates as the polyox solutions, is probably of little analytical
value. It does provide some measure of the degree of viscous relaxation
in a frequency range. As shown by Figure 7, there may also be some
direct relationship between this viscosity and that obtained by rota-
tional instruments if the shear rate of the latter is equivalent to
the angular frequency of the oscillating device. Figure 7 shows that
the general shape of the Brookfield viscosity data and the apparent
viscosity data from the oscillators is the same. It is further clear
that 118cps in an oscillatory system corresponds to a rotational speed
well in excess of 30rpm,or conversely, that 30rpm corresponds to a
frequency well below 100cps. However, such an equivalence is probably
more likely to hold for the real part of the complex viscosity, if it
holds at all.

The frequency range covered during these investigations was too
narrow to describe quantitatively the viscoelastic behavior of the
polyox solutions as functions of frequency. However, the pattern
observed in this limited region is consistent with that observed in
other polymer solutions, i.e. the viscous effects are reduced and the
elastic effects become more pronounced as the frequency increases.

Chester measured the shear modulus of 0.1 and 0.5 percent polyox
respectively at a frequency of seven megacycles per second. The real
parts of the complex shear modulus for these concentrations measured
at 118 and 439cps were 0.55 and 5.13 dynes per square centimeter, and

42.5 and 79.1 dynes per square centimeter respectively. Measurements taken at intermediate frequencies between these extremes would be required to verify the compatibility of these values.

The accuracy of the measurements taken with the torsional oscillator can be inferred from the reproducibility of the measurements, and the "goodness-of-fit" of the calibration curves. The maximum standard deviation of the decay rates in any fluid, including air, was two percent. The reproducibility of measuring changes in frequency due to a liquid loading was 0.001cps for the 439cps oscillator, and 0.0001cps for the 118cps oscillator. The standard deviations of the slope for the best fitting line for the calibration curves can be seen in Table 3. The maximum standard deviation is about 1.6 percent of the slope.

Based on the accuracy of the basic measurements, the error in the computed viscosities and shear moduli is no more than five percent of the tabulated values, with an "average" error of about 3.5 percent. The values of η_1 and η_2 for the 439cps oscillator in Table 1, and of η_a in Table 2, are shown with maximum possible error for reference.

6. Discussion of Results

It is apparent from the measurements taken at the frequencies
of 118, 439, and 675cps that a viscous relaxation phenomenon does
occur for all aqueous polyox solutions of concentration 0.1 to 3.0
percent in this frequency region. It can be assumed from the fact
that the viscosities measured by capillary tubes and a Brookfield
viscometer were considerably greater than those measured at 118cps
that some definite viscous relaxation process must occur at even lower
frequencies. Also, since the viscosities measured in this frequency
range are greater than those observed by Chester (whose tests were
made in the 10 megacycle range), further relaxation must occur at
higher frequencies.

Assuming an equivalence between shear rate and angular frequency,
the measurements made with the Brookfield viscometer indicate that
viscous relaxation may be observed for frequencies on the order of
0.1cps (4). (This number was determined by estimating the rate of
shear for the Brookfield viscometer in 0.5 and 1.0 percent solutions.
The estimate is based on the measured viscosity, the known dimensions
of a spindle, and the measured torque. The shear rate is estimated by
dividing the shear stress by the measured viscosity.)

One model for a relaxation phenomenon involving a viscosity η
and a shear modulus G is that of a Maxwellian element. A Maxwellian
element is defined as a spring (representing the shear modulus) and
dashpot (representing the viscosity) in series. If η_o is the zero
shear rate viscosity, ω the frequency of disturbance applied, then,
for simple harmonic excitation, (1, 9):

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$$\eta_1 = \frac{\eta_0}{1 + \omega^2 \tau^2}$$

where relaxation time $\tau = 2\pi \eta_0 / G_\infty$,

and $\quad\quad\quad\quad \eta_1$ = the "relaxed" viscosity

$\quad\quad\quad\quad G_\infty$ = shear modulus at infinite shear.

Solving this equation for η_0 and τ by using the values of η_1 and ω determined in these investigations leads to inconsistent results, i.e. the calculated zero shear rate is considerably less than the observed "low shear rate" viscosities measured with the Brookfield. This indicates that the simple Maxwellian element is not applicable to the complicated polyox solutions. If it is assumed that the properties of the polyox solutions can be represented by a combination of Maxwellian elements (10, 21), these results further indicate that some distrebution of relaxation times and relaxation frequencies exist. Measurements at both lower and higher frequencies than those reported herein are required to ascertain the nature of such a distribution.

Porter and Johnson have stated that conventional capillary viscosities closely define limiting low-shear viscosities (16). For the polyox solutions, the observed viscosities measured by capillary tubes varied considerably depending upon the dimensions of the capillary. (As much as a 50 percent variance in viscosities was observed.) These viscosities were also lower than those measured by the Brookfield instrument. Thus, this method of determining low shear limits is not satisfactory for polyox solutions of concentrations greater than 0.1 percent. (See Table 2 for a comparison of apparent viscosities measured by the different methods.)

7. Acknowledgements

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118cps

Conc.	η_1	η_2	$|\eta^*|$	G_1	G_2	$|G^*|$
0.10	1.71	0.0742	1.71	0.55	12.6	12.6
0.25	3.80	1.91	4.25	14.2	28.2	31.5
0.50	8.98	5.73	10.6	42.5	66.5	78.9
0.75	16.2	12.0	20.2	88.9	120.	149.
1.0	27.1	19.1	33.2	142.	201.	246.
2.0	103.	76.1	128.	564.	765.	950.
3.0	310.	234.	388.	1740.	2300.	2880.

439cps

Conc.	η_1	η_2	$|\eta^*|$	G_1	G_2	$|G^*|$
0.10	1.41±0.09	0.186±0.07	1.42	5.13	38.9	39.2
0.25	2.55±0.10	0.872±0.09	2.70	24.0	70.3	74.3
0.50	4.17±0.20	2.87±0.50	5.06	79.1	115.	140.
0.75	6.62±0.25	5.57±0.40	8.65	154.	182.	238.
1.0	9.08±0.30	8.81±0.40	12.6	243.	250.	349.
2.0	19.3±0.45	36.9±1.0	41.6	1020.	533.	1150.
3.0	24.9±0.70	80.6±2.5	84.4	2220.	686.	2880.

Table 1. Viscosities and Shear Moduli for Polyox Solutions. The η's are in centipoise, the G's are in dynes/cm^2, and concentrations are in weight percent.

a. Apparent Viscosity as Measured by Torsional Oscillators

Concentration	118cps	439cps	675cps
0.10	1.78	1.61±0.06	1.47
0.25	6.16	3.57±0.08	3.20
0.50	16.4	7.94±0.20	6.87
0.75	32.1	14.3±0.3	13.8
1.0	52.2	21.5±0.5	18.6
2.0	204.	78.4±3.0	-
3.0	622.	165.±5.0	-

b. Apparent Viscosity as Measured by Capillary Tube and
    Brookfield Viscometers

Concentration	Oswald	Fenske-Cannon	6.0rpm
0.10	3.35±0.02	2.71±0.02	4.15
0.25	14.8±0.2	11.5±0.2	20.0
0.50	77.6±0.2	69.5±0.2	158.0
0.75	-	-	592.5
1.0	-	-	1430.
2.0	-	-	10,100.
3.0	-	-	48,000.

Table 2. Apparent Viscosities, in Centipoise

Freq.(cps)	Q	K_α	Standard Deviation	K_ω	Standard Deviation
118	21,600	0.02045	0.00014	0.0260	0.00042
439	9,190	0.0365	0.00032	0.0353	0.00028
675	9,680	0.0379	0.00037	- -	- -

Table 3. Constants for Torsional Oscillators

Figure 1. Block Diagram Showing Experimental Setup for Measurements Using Torsional Oscillator.
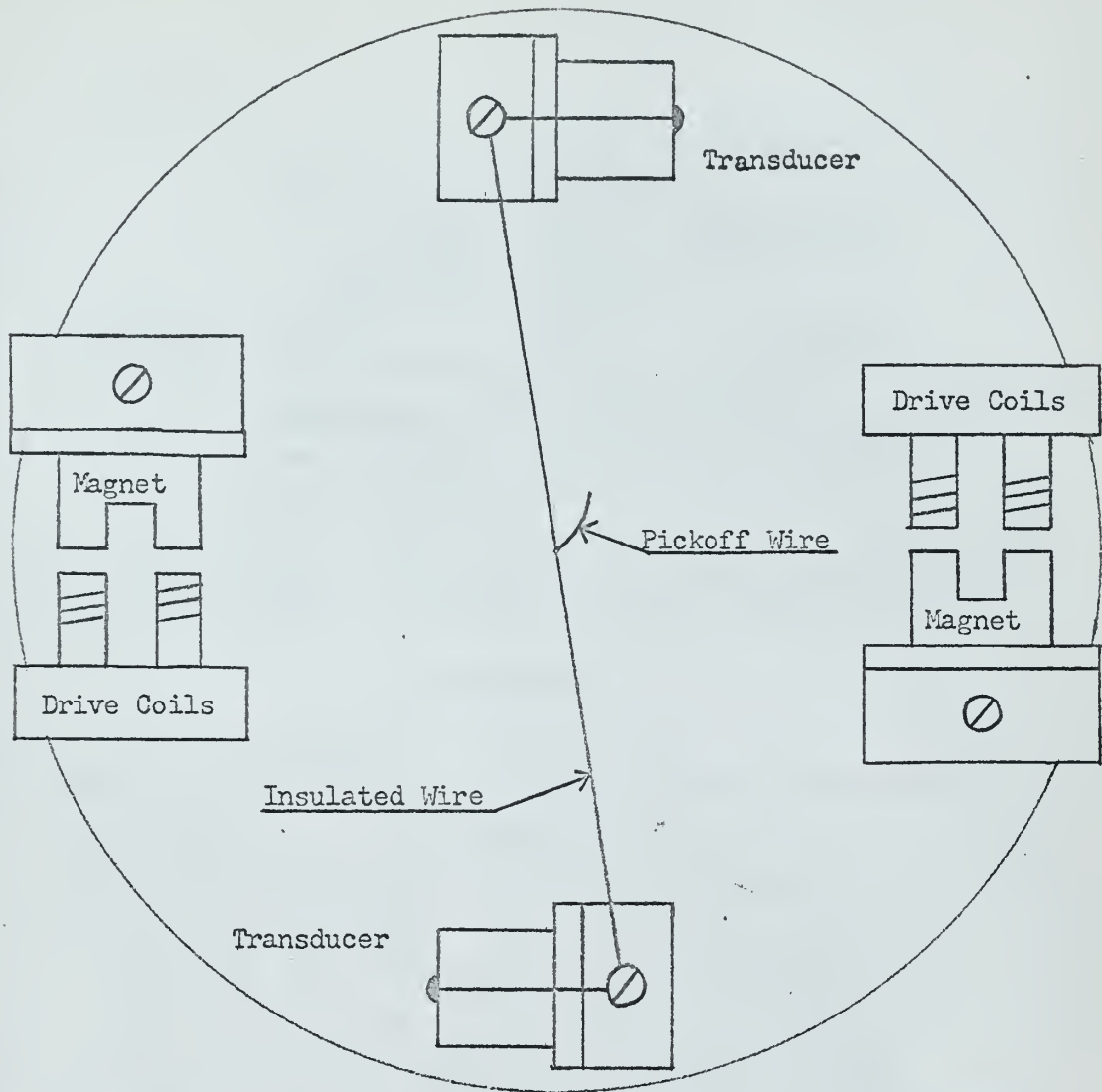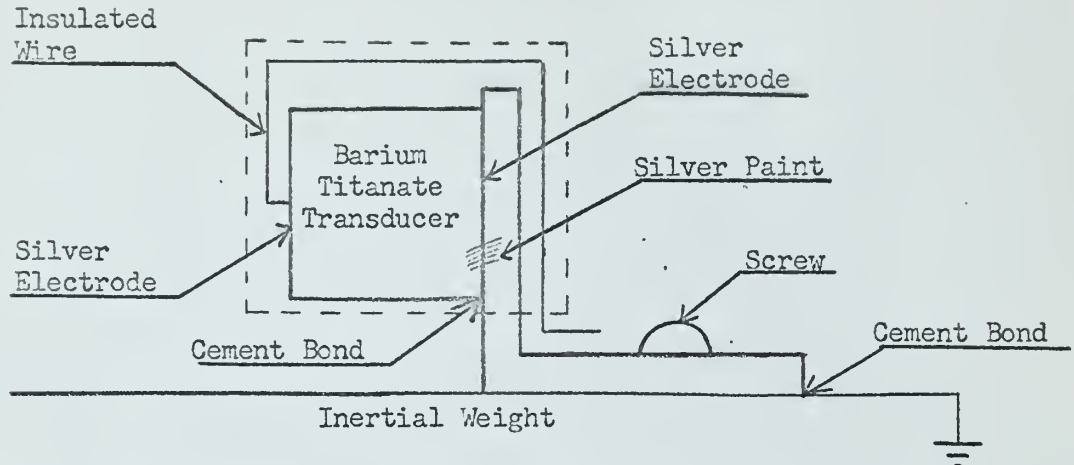
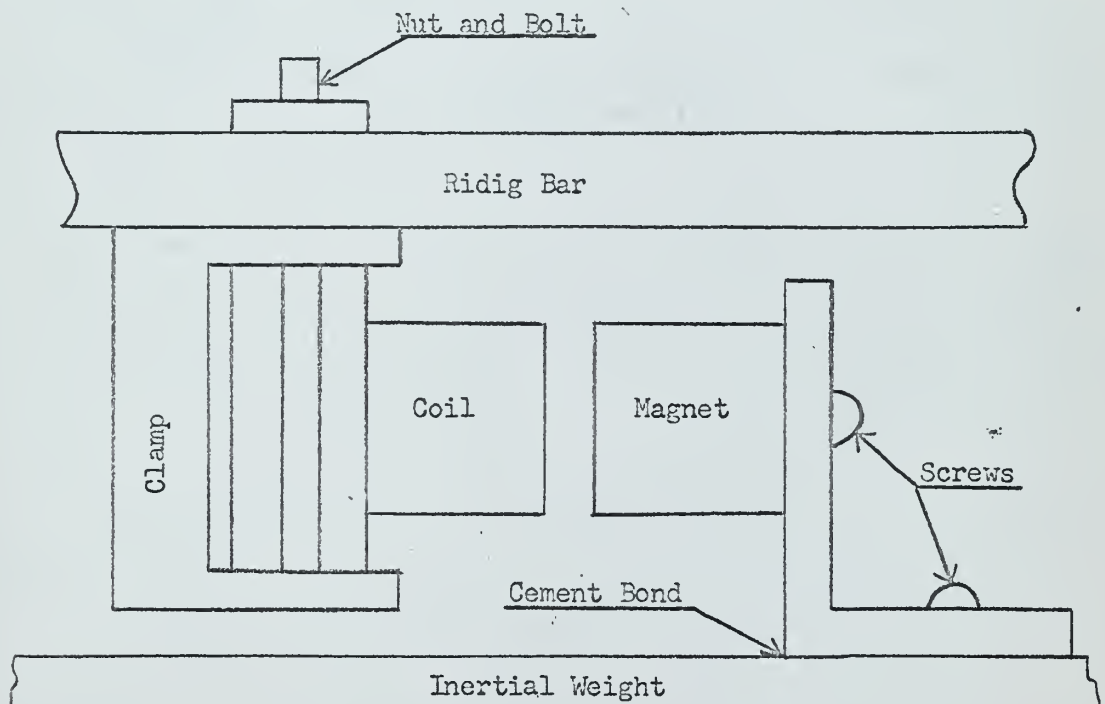Figure 2. Schematic of Torsional Oscillator Assembly
(Not to scale)

Figure 3. Top View of Upper Inertial Weight. Rigid bar for holding
Drive Coils is not shown. Insulated lead wire was cemented to
top of inertial weight, then coated with silver paint to provide
grounded electrical shielding. Connection to the pickoff wire
was through a fine coiled wire, shielded with a metal umbrella.

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Detail of Transducer. Portion inside dashed line was coated first with insulating film, then with coat of silver paint to ground.

Detail of One Drive Coil and Magnet.

Figure 4. Schematics of Barium Titanate Transducer and Electro-Magnetic Drive. Not to scale.

Calibration Curves for 439 cps. Oscillator
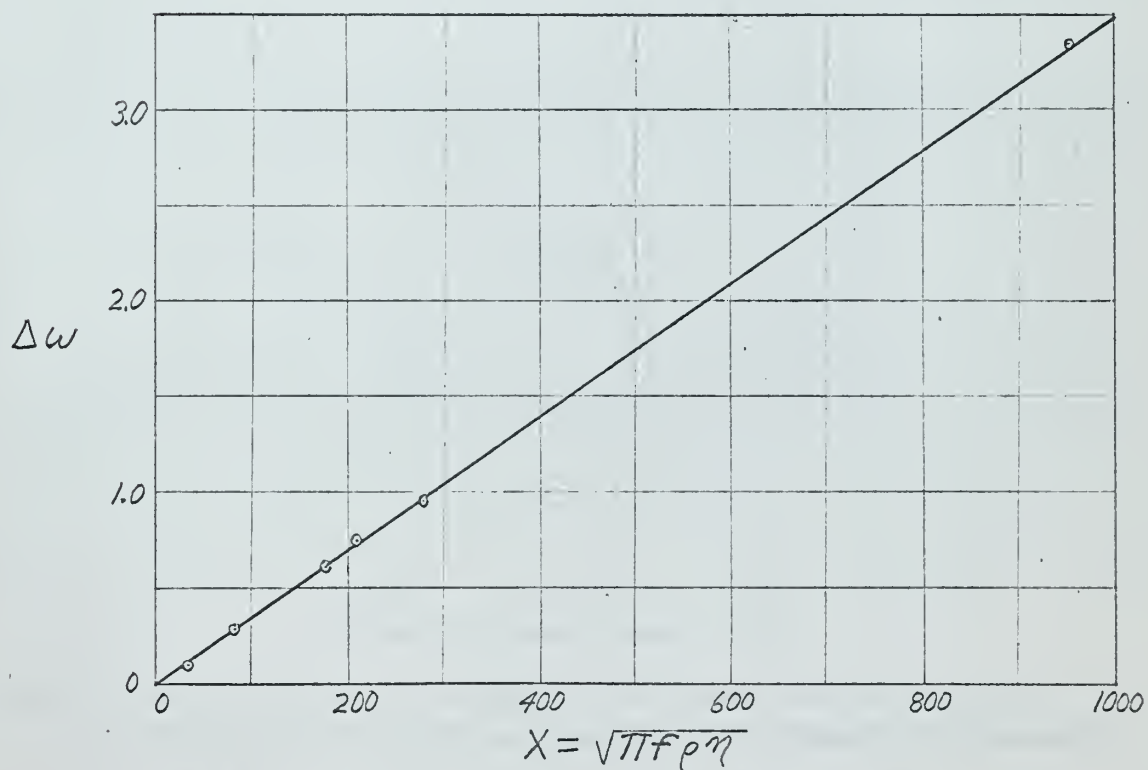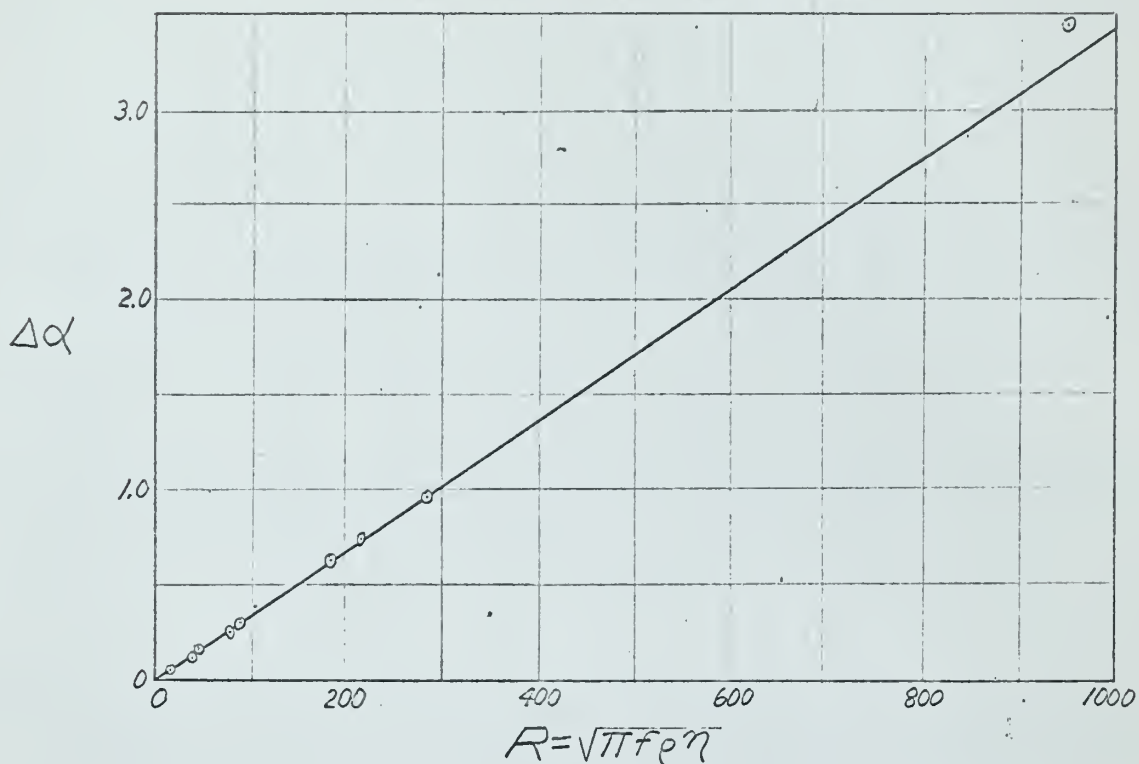
using Standard Newtonian Liquids

Figure 5. Typical Calibration Curves for Torsional Oscillator.

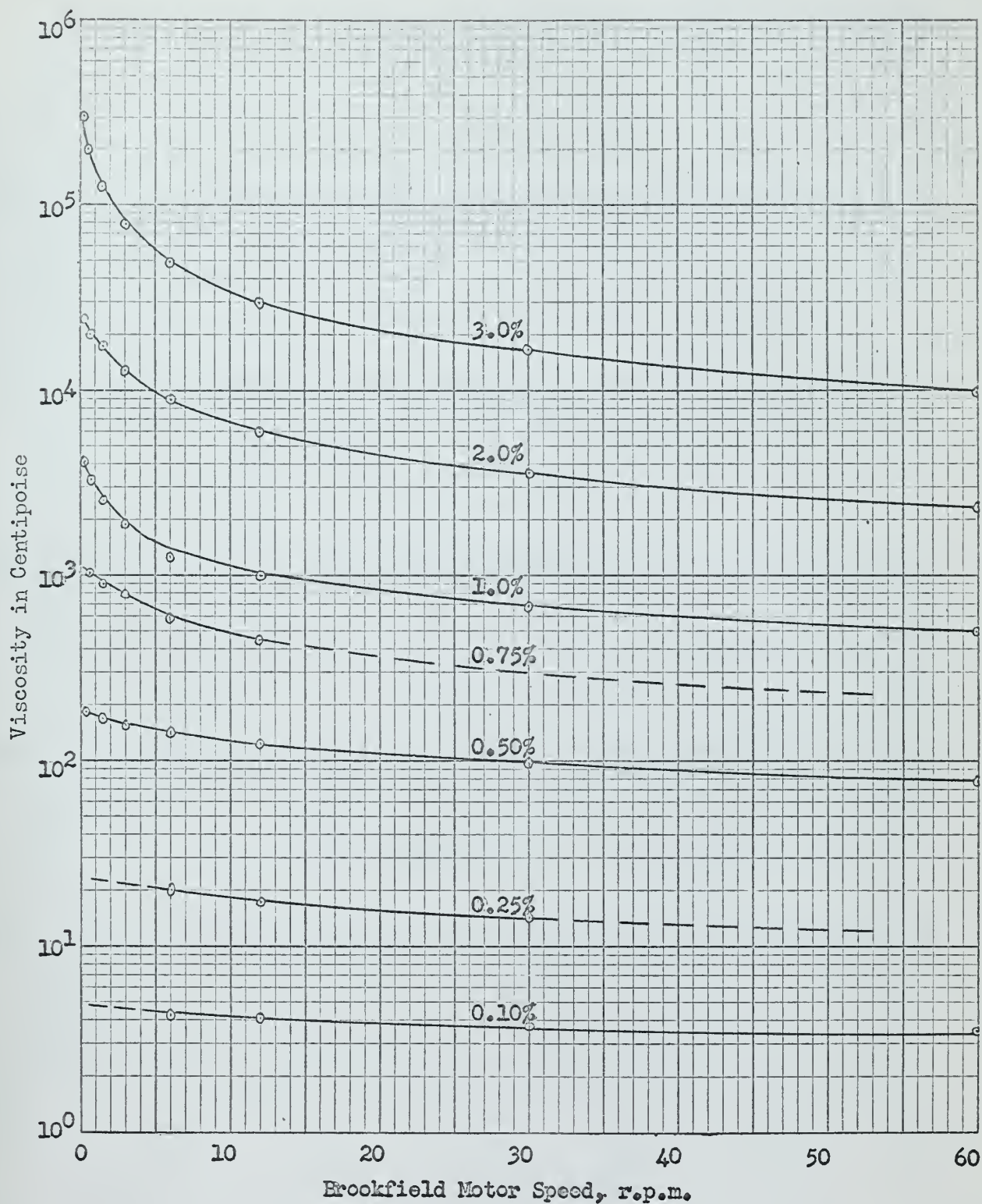Straight lines are least-square-error fits.

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Figure 6. Plot of Apparent Viscosity versus Shear Rate for Various
Polyox Concentrations as measured by the Brookfield Viscometer.
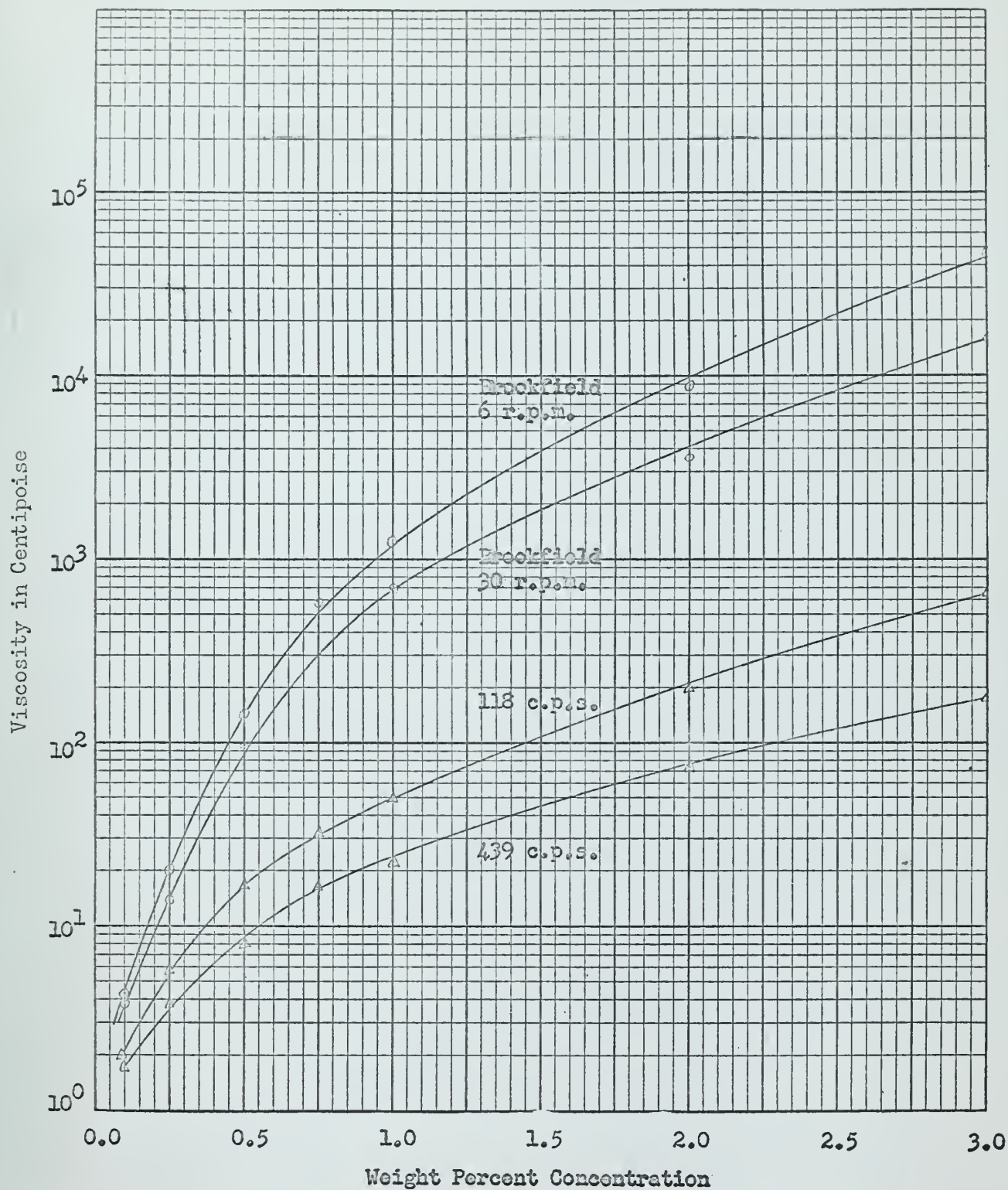
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Figure 7. Plot of Apparent Viscosity versus Polyox Concentration for
Various Shear Rates as measured by Brookfield Viscometer
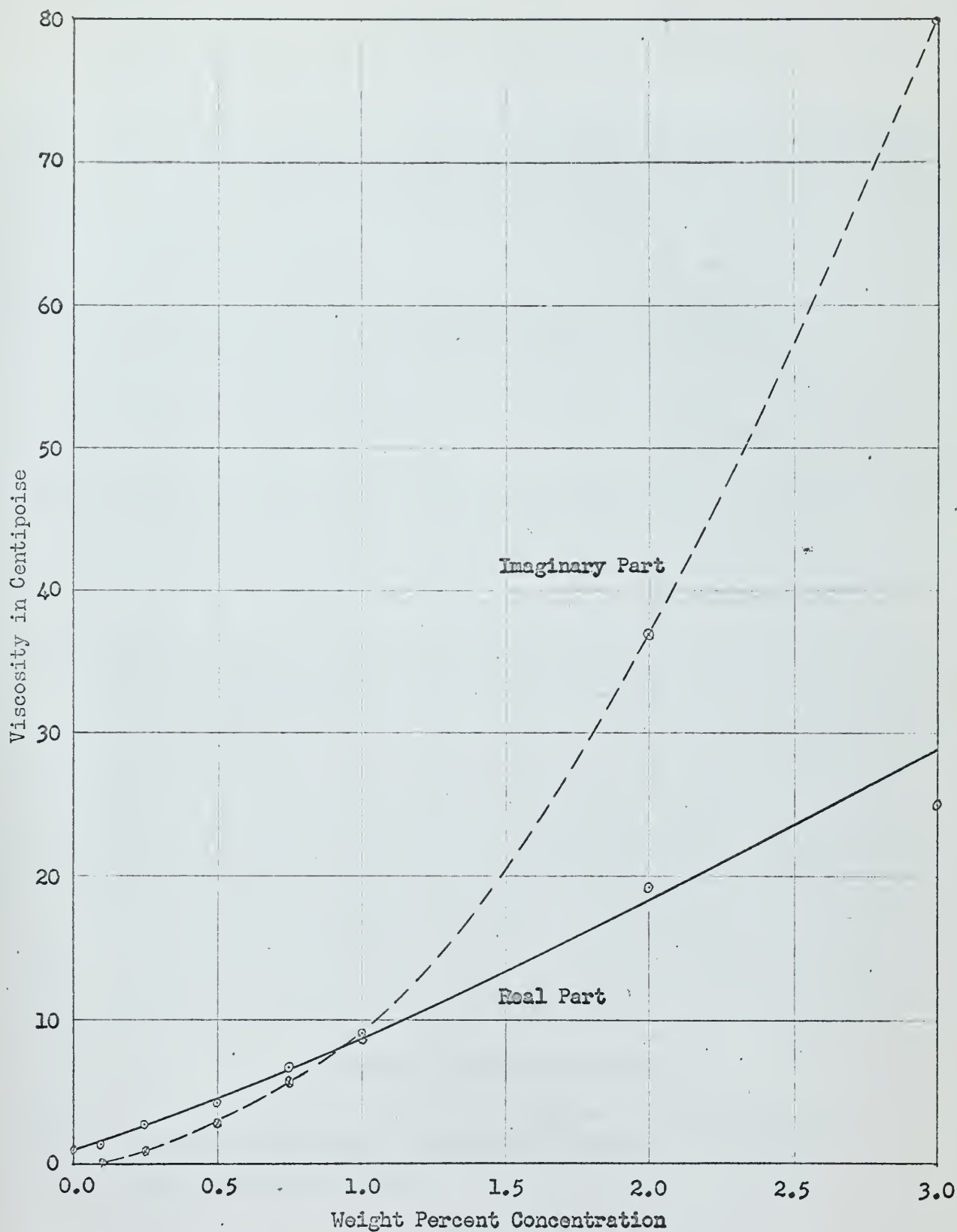and Torsional Oscillators.

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Figure 8. Plot of Components of the Complex Viscosity versus Polyox
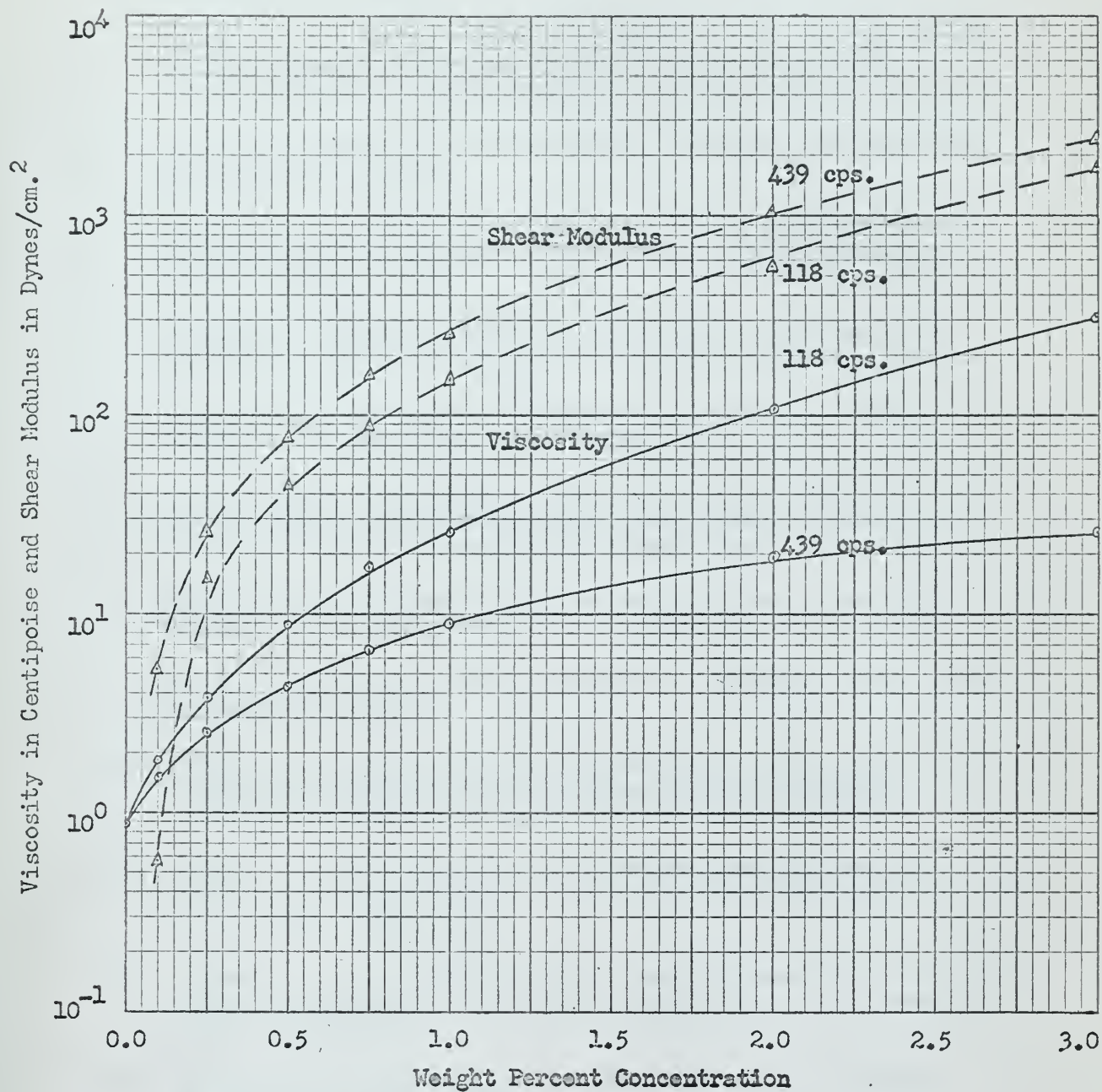Concentration measured at 439 cycles per second.

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Figure 9. Plot of the Real Parts of the Complex Viscosity and Shear Moduli versus Polyox Concentration measured at 118 and 439 cycles per second.

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